

Proceedings of the American Academy of Arts and Sciences.

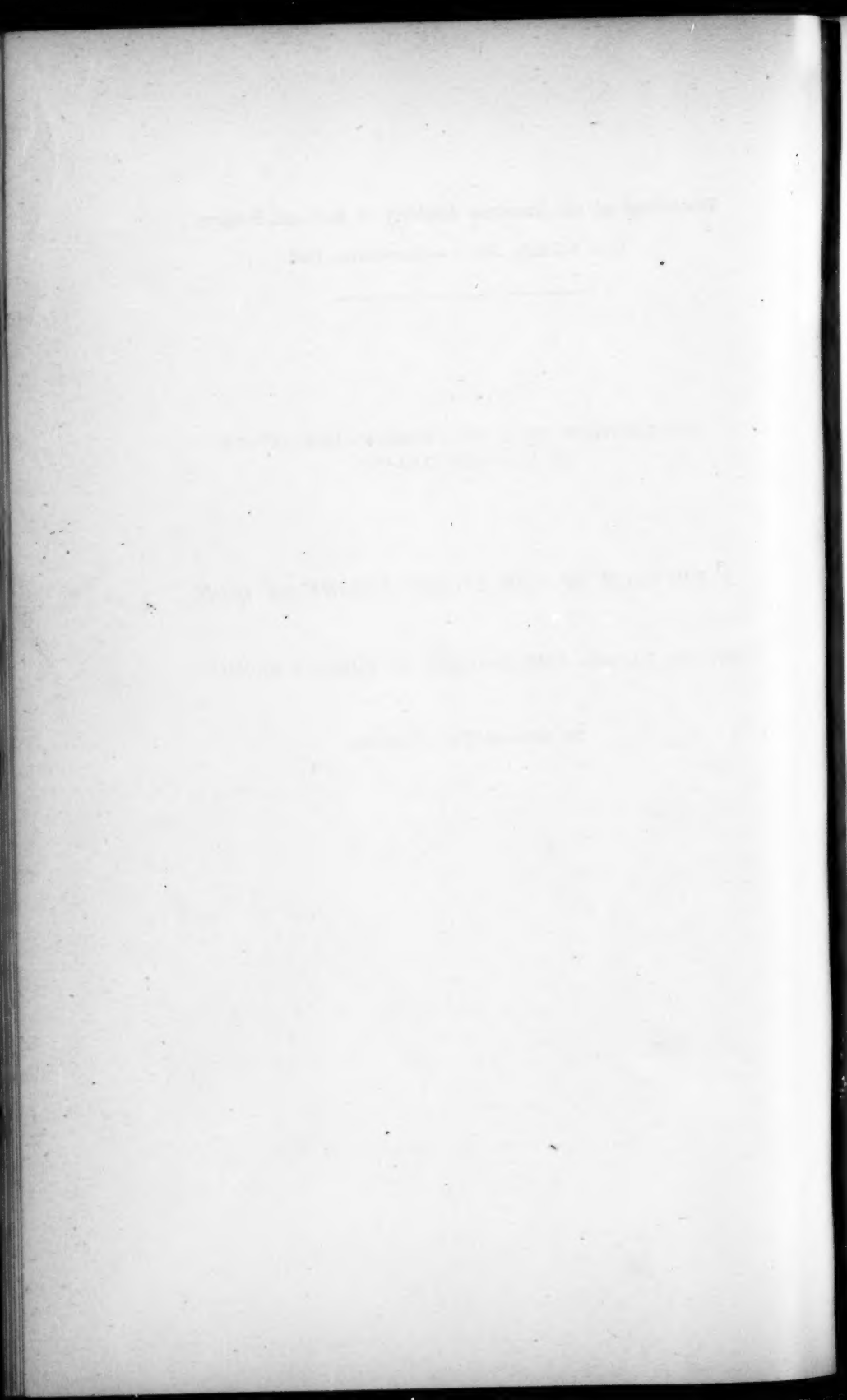
VOL. XXXIX. No. 9. — NOVEMBER, 1903.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF IRON.

SECOND PAPER.—THE ANALYSIS OF FERROUS BROMIDE.

BY GREGORY PAUL BAXTER.



CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF IRON.

SECOND PAPER.—THE ANALYSIS OF FERROUS BROMIDE.

By GREGORY PAUL BAXTER.

Presented by T. W. Richards, October 14, 1903. Received October 3, 1903.

FOUR years ago a determination of the atomic weight of iron, made in this laboratory by reduction of the oxide in hydrogen, led to the value 55.883 ($O = 16.000$).^{*} Since the atomic weight in use at that time, 56.02, differs so materially from the above value, it seemed advisable to redetermine the constant in question by a radically different method.

Bromides may be analyzed with the greatest ease and exactness, provided they can be obtained in a state of purity. Since ferric bromide is far too unstable at high temperatures to permit thorough drying of the salt, ferrous bromide was chosen as the substance for analysis. This salt rapidly oxidizes in the presence of moist air; but the ease with which ferric bromide is decomposed by heat into ferrous bromide and bromine is an advantage in the preparation of ferrous bromide, for it proved possible completely to free the latter salt from ferric impurity by subjecting it to a high temperature in an atmosphere of dry hydrobromic acid gas.

Ferrous bromide was prepared by heating metallic iron in a current of dry nitrogen and hydrobromic acid gases, at a temperature sufficiently high to sublime the resulting salt. When the salt was removed from the sublimation tube, it necessarily came in contact with moist air, and thus become covered with a thin coating of ferric salt. It was then subjected to prolonged heating in a current of dry nitrogen and hydrobromic acid gases. In order to determine whether the ferric salt was thus decomposed, samples of the product were dissolved in a freshly boiled, acid solution of ammoniac sulphocyanate. If the hydrobromic acid and

^{*} Richards and Baxter, These Proceedings, 35, 253.

ferrous bromide contain no chlorine, the salt obtained in the above manner gives a barely perceptible coloration with the sulphocyanate, showing that reduction is complete. On the other hand, if the ferrous bromide was prepared from commercial bromine, it was never found possible to eliminate completely the ferric salt; although by colorimetric comparison with standard ferric solutions to which ammoniac sulphocyanate had been added, it was shown that the proportion of iron in the ferric state did not amount on an average to more than two hundredths of one per cent. The greater difficulty with which ferric chloride is reduced is doubtless the cause of this difference in behavior of the two varieties of material.

The apparatus with which these operations were carried out was essentially that used for similar purposes in the determinations of the atomic weights of cobalt,* nickel,† and uranium‡ in this laboratory. A mixture of air and ammonia was passed over heated rolls of copper gauze and the excess of ammonia was removed by means of sulphuric acid. The partially dried gas, after bubbling through bromine in a small flask, was conducted through hydrobromic acid in which was suspended red phosphorus to convert the bromine into hydrobromic acid. Suitable desiccating agents then dried the mixture of gases. Pure iron, contained in an unglazed porcelain boat, was placed in a porcelain tube heated by a Fletcher furnace. The mixed nitrogen and hydrobromic acid gases were passed over the hot iron, forming ferrous bromide, and since the temperature was high enough to sublime the ferrous bromide, the salt was carried along by the current of gases to be deposited in a smaller cool porcelain tube which telescoped into the larger tube. As soon as the inner end of the smaller tube was stopped up with bromide, the furnace was allowed to cool for some time, and the sublimed salt while still warm was transferred to a weighing bottle. The portions next the porcelain were never collected for analysis. The ferrous bromide, contained in a platinum boat, was then heated to about 400° C. in a current of nitrogen and hydrobromic acid gases for an hour or more. Finally, after the boat had become cool, these gases were displaced, first by nitrogen, then by dry air, and the boat was transferred to a weighing bottle without exposure to moisture, by means of the bottling apparatus so frequently used for the purpose in this laboratory. §

* Richards and Baxter, These Proceedings, **33**, 117.

† Richards and Cushman, These Proceedings, **33**, 99.

‡ Richards and Merigold, These Proceedings, **37**, 378.

§ Richards and Parker, These Proceedings, **32**, 59.

As has been stated before, ferrous bromide prepared in this way does not contain a weighable amount of ferric salt, and is a perfectly stable substance in dry air. The pure salt varies in color from light yellow to dark brown, according to the thickness of the crystals.

In several cases the platinum boat which contained the salt during the drying became covered with a black film, which disappeared when the boat was ignited, without producing any change in weight. Since a similar difficulty had never been met before when a platinum boat was heated in hydrobromic acid, the phenomenon was at first ascribed to the presence of either ferrous or ferric salt; but the eventual conversion of the platinum into a brittle condition seemed to indicate some other cause of the difficulty. The presence of phosphorus compounds in the mixed gases was suspected, and when tests were made with ammonic molybdate, both in the salt and in hydrobromic acid which had been generated in the apparatus and collected in water, traces of phosphoric acid were found in both cases. The source of the phosphoric acid was easily discovered.

Whenever bromine is passed for a sufficiently long time into a solution of hydrobromic acid containing red phosphorus, a yellow crystalline deposit is formed upon the walls of the flask above the solution. This yellow substance resembles the pentabromide of phosphorus in appearance and gives off much hydrobromic acid when treated with water, hence it must have been the pentabromide. Since at ordinary temperatures the pentabromide is not volatile while the tribromide is volatile, probably the formation of pentabromide is due to volatilization of the tribromide from the solution and consequent conversion into pentabromide by bromine which escapes reduction in bubbling through the flask. Obviously the formation of either substance in appreciable quantity is impossible so long as the solution in the flask is very aqueous. The aqueous tension of the solution is never high, however, since the concentration of the hydrobromic acid is at a maximum, and the aqueous tension is diminished still farther as the concentration of phosphorous and phosphoric acids in the solution increases. Eventually, then, the aqueous tension of the solution should be such as to make possible the existence of the bromides of phosphorus. The attacking of the boat was evidently due to the presence of compounds of phosphorus in the mixed gases.

In order to remove the traces of bromine which escaped reduction in the first flask, containing hydrobromic acid and phosphorus, the gases, after passing through this flask, were always conducted through a short U-tube containing these same substances. The concentration

of acids of phosphorus never became high in this U-tube, but it was evident that a single such tube was not enough to remove the bromides of phosphorus completely. Consequently a second U-tube, filled with beads moistened with hydrobromic acid, was inserted, and pains was taken that no very considerable concentration of acids of phosphorus should ever exist in the hydrobromic acid generating flask. After this modification of the apparatus had been made, the boat remained absolutely unchanged in appearance and weight.

These phenomena became very evident in the present work because such large quantities of hydrobromic acid were necessary for the synthesis and sublimation of ferrous bromide. Also, since the bromide was condensed from an atmosphere of the gas, the conditions were those capable of causing the retention of a maximum amount of phosphorus. In the cases of the cobaltous and nickelous bromides, on the other hand, synthesis was effected by means of *bromine* vapor, very little hydrobromic acid being used in their preparation. It was only during the drying of the salts that they came in contact with hydrobromic acid for any considerable length of time, and even then the contamination could have been only superficial. As a matter of fact, it was found impossible at the time to detect the slightest trace of phosphorus in either of the two bromides.

Considerable difficulty was experienced in obtaining ferrous bromide which would give a clear solution in water. The earlier samples contained, besides silica from the new porcelain tubes, a slight black residue which became red upon ignition, and which may have been the magnetic oxide of iron. The amount of this residue was very much diminished by a lavish expenditure of hydrobromic acid during sublimation. These residues were filtered upon tiny filter papers, ignited, and weighed. In none of the samples used for analysis did the weight of the insoluble residue amount to more than one thirtieth of a per cent of the weight of the salt. Even in the best material the insoluble residues contained traces of phosphoric acid. In Analysis 2 (p. 252) the phosphoric acid in the residue was determined by precipitation with ammonic molybdate to be 0.0001 gram. It was easily shown, however, that all the phosphoric acid was in the insoluble residue, for in Analysis 4 the filtrate from the silver bromide was evaporated to small bulk and treated with ammonic molybdate, without the formation of a visible amount of precipitate. Evidently no error was introduced into the analysis by the presence of the phosphoric acid.

The determination of the bromine in the salt offered certain difficulties

owing to the fact that ferrous salts precipitate silver from its solutions under certain conditions. Obviously it was necessary to oxidize the ferrous bromide solution before addition of the silver nitrate. Hydrogen peroxide proved too slow an oxidizing agent at ordinary temperatures, potassium permanganate is too vigorous in its action, and sets free bromine from the salt. Even potassium dichromate, at concentrations such as are used in ordinary analytical work, sets free bromine rapidly. But if a very dilute solution of dichromate is used, and if the sulphuric acid is added gradually with the dichromate and only in quantities theoretically necessary, so as to keep the velocity of reaction as low as possible, and finally if the solution of dichromate and sulphuric acid is introduced beneath the surface of the solution of ferrous bromide, so that any bromine set free may be taken up by the ferrous salt before it can escape from the solution, oxidation can be accomplished without the loss of enough bromine to be detected with starch iodide paper. Furthermore complete oxidation is unnecessary, for although dilute solutions of ferrous and silver salts deposit silver upon standing, if considerable ferric salt is present no precipitation of silver takes place owing to the retarding influence of the ferric salt.

PURIFICATION OF MATERIALS.

Pure ferric oxide was prepared in an exactly similar fashion to that used in the previous investigation upon the oxide.* In order to convert this oxide into the metal, one portion was heated in a current of ammonia. But since metal reduced by ordinary ammonia, when dissolved in sulphuric acid, leaves a residue of carbon owing to the presence of amines in the ammonia, the material used in all analyses except Analysis 1 was reduced in pure electrolytic hydrogen.†

Silver was purified in the manner usually employed in this laboratory, except that the electrolytic crystals were finally fused in a current of pure hydrogen instead of in a vacuum. Even spongy silver occludes no appreciable amount of hydrogen when heated in this gas,‡ hence no error could have resulted from this source.

Bromine was partially freed from chlorine by solution in concentrated aqueous calcic bromide made from a portion of the same sample of bromine. It was then converted into hydrobromic acid by means of

* Richards and Baxter, These Proceedings, 35, 256.

† These Proceedings, 34, 357.

‡ Baxter, Amer. Chem. Jour., 22, 362.

washed red phosphorus and water, and the resulting hydrobromic acid, which contained a considerable excess of bromine, was freed from iodine by distilling off this bromine. After several distillations the hydrobromic acid was converted into bromine by treatment with recrystallized potassium permanganate. The resulting bromine was thus distilled a second time from a solution of a bromide of much greater purity than in the first case. Analysis of this bromine was carried out by precipitating a known weight of silver with a slight excess of ammoniac bromide made from this bromine.

Weight of Silver in Vacuum.	Weight of fused Silver Bromide in Vacuum.	Ratio Ag : AgBr.
grams. 4.77783	grams. 8.31754	57.4428
5.87977	10.28533	57.4459
4.82995	8.40809	57.4441
Average 57.4443		

This value is almost identical with the average of Stas's experiments, 57.4445, and shows conclusively that both bromine and silver were pure.

METHOD OF ANALYSIS.

The method of analysis was as follows. The salt was dissolved in water which had been slightly acidified with sulphuric acid to prevent the formation of insoluble basic ferric salt, and the trace of insoluble residue was collected upon a small filter paper and determined as previously described. The solution of ferrous bromide, which had been diluted to a volume of at least four hundred cubic centimeters by the wash waters, was then oxidized by adding slowly, through a funnel tube with a fine tip which dipped below the surface of the solution, slightly less than the calculated amount of a solution of potassic dichromate. This solution contained one and one-half grams of potassic dichromate in a liter of solution, together with a slight excess of the quantity of sulphuric acid necessary to complete the reaction. The dichromate had been recrystallized from the purest water, and the sulphuric acid had been redistilled, so that no halogens could have been contained in the oxidizing solution. In Analyses 1 and 2 an excess of the calculated

quantity of pure silver was dissolved in pure nitric acid and the solution, after dilution, was added slowly to the bromide. The resulting silver bromide was filtered upon a Gooch crucible, heated to 200° in an electric oven, and weighed. The asbestos shreds which passed through the crucible, together with any accompanying silver bromide, were collected upon a small filter. This filter was then ignited, the ash treated with a drop of a mixture of pure nitric and hydrobromic acids, and finally the weight of the residue determined. After the weight of the silver bromide had been found, it was fused in a porcelain crucible and the loss in weight determined. In Analyses 5 and 6 exactly the calculated amount of silver was used in the precipitation, and portions of the clear solution above the precipitate were tested with solutions of hydrobromic acid and silver nitrate in a nephelometer kindly loaned for the purpose by Mr. R. C. Wells. In both analyses a very slight opalescence was produced to the same extent in both portions, showing that the exact amount of silver necessary to combine with the bromine had been added. The absence of any appreciable amount of precipitate in either portion is evidence that no chlorine was present in the salt; for silver chloride, owing to its greater solubility, would have made itself evident by a considerable cloudiness in the nephelometer test. In these two analyses an excess of silver nitrate was then added and the weight of the silver bromide was determined (Analyses 3 and 4).

In order that the weight of the ferrous bromide might be reduced to a vacuum standard, its specific gravity was found by determining the weight of kerosene displaced by a known quantity of salt. The kerosene was first dried by means of stick soda, and then distilled. The portion distilling between 200° and 240° was used in the determinations. Its specific gravity at 25° referred to water at 4° was found to be 0.7693.

Weight of Ferrous Bromide in Vacuum.	Weight of Kerosene in Vacuum.	Specific Gravity of Ferrous Bromide - $25^{\circ}/4^{\circ}$.
grams. 2.9660	grams. 0.4918	4.639
2.5712	0.4260	4.643
3.3619	0.5592	4.625
Average		4.636

Accordingly, to every apparent gram of ferrous bromide a vacuum correction of 0.000118 gram was added. The vacuum correction of silver bromide was assumed to be +0.000046, and that of silver to be -0.000031. The atomic weights used in the calculations are: Oxygen, 16.000; Bromine, 79.955; and Silver, 107.93.

The weights, which were of brass, platinum plated, were carefully standardized to hundredths of a milligram.

Number of Analysis.	Weight of Ferrous Bromide in Vacuum.	Weight of Residue.	Weight of Silver Bromide in Vacuum.	Loss on Fusion.	Weight of Asbestos.	Weight of Silver in Vacuum.	Atomic Weight of Iron.
	grams.	grams.	grams.	grams.	grams.	grams.	
1	3.55996	0.00067	6.19852		0.00021		55.856
2	3.07566	0.00118	5.35453	0.00080	0.00027		55.852
3	2.96128	0.00026	5.15706	0.00020	0.00010		55.849
4	4.00816	0.00025	6.97966	0.00013	0.00030		55.862
5	2.96128	0.00026				2.96234	55.854
6	4.00816	0.00025				4.00987	55.871
Average							55.857

Both ferric and chromic salts show a tendency to be occluded by precipitates, and it was feared that difficulty might arise from this source. The close agreement of the results obtained by weighing the silver bromide with those calculated from the weight of the silver shows that no error of the sort actually existed. The ratios of silver to silver bromide in the two analyses in which both substances were determined are 57.444 and 57.442.

One point remains to be considered, — the presence of alkaline bromides in the salt. All bromides made by sublimation in porcelain tubes have been shown to contain sodium bromide in appreciable quantities. An attempt was made to determine the amount of this impurity by reducing the ferrous bromide in hydrogen and subsequently leaching out the soluble salts remaining. This method was used in the cases of cobalt and nickel, and afforded at the same time a means of determining the per cent of metal in the salt. Unfortunately the method was not practicable in this case, for although ferrous bromide is slowly reduced in

moist hydrogen, it is a very difficult matter to avoid considerable sublimation of the salt during the process, and complete reduction could be obtained only at a temperature at which all the sodic bromide sublimes out of the boat. Recourse was taken to the method of precipitating the iron from a solution of the salt with ammonia, and determining the sodium in the filtrate. The solution of sodium and ammonium bromides was evaporated to dryness, and after the ammonium salts had been volatilized by gentle ignition, the residue was taken up with water and again evaporated with a slight excess of sulphuric acid. Finally the residue was ignited in a stream of ammonia. These operations were carried out entirely in platinum vessels, and the water used was condensed in a block tin condenser and collected in platinum. The residues obtained in this way gave no test for any metal except sodium when examined spectroscopically.

Weight of Ferrous Bromide.	Weight of Sodic Sulphate.	Weight of Sodic Bromide Calculated.	Per cent of Sodic Bromide.
grams. 4.553	grams. 0.0050	grams. 0.0073	0.160
6.311	0.0051	0.0074	0.117
Average			0.138

Although the porcelain tubes were exactly similar to those used in the sublimation of cobalt, nickel, and uranium bromides, the amount of the alkaline impurity is slightly larger than that found in those cases. Presumably this difference is due to the unglazed porcelain boats, which it was hoped would be more resistant to the action of hydrobromic acid gas, but which were attacked very badly during the sublimation. The attacking of the boat may have been due to the fact that the ferrous bromide fused in the boat while the other bromides did not fuse to a noticeable extent.

Since in the cases of cobalt and nickel, where the question of impurity introduced from the porcelain tubes was sifted to the bottom, sodium was the only metal found, it is reasonable to conclude that here also sodium was the only impurity. Sodium bromide contains a higher percentage of bromine than ferrous bromide, hence the weights of silver and silver bromide determined by analysis of the sublimed salt are slightly too

large. 1.00000 gram of salt yielded 1.74155 grams of silver bromide. Of this silver bromide, 0.00252 gram correspond to 0.00138 gram of sodium bromide contained in the salt. If both these corrections are subtracted, the atomic weight of iron calculated from the quantities remaining is 55.871.

This value is slightly lower than the result of the analysis of ferric oxide, 55.883. But this was to be expected, for it was pointed out at the time the earlier results were published, that the value obtained was rather too high than too low, since the errors which would affect determinations made by reduction of the oxide, i. e., those due to the presence of non-reducible impurities in the material and to incomplete reduction, would have raised the atomic weight above its true value. As a matter of fact, it was found impossible to prove that either of these errors existed. Occluded gases, which would have produced the opposite effect, were conclusively proved to be absent. It is interesting to note that Analysis 6 of the earlier series, in which most material was used and which consequently should be the most accurate, gave a result, 55.870, practically identical with that of this research. On the other hand, the presence in the ferrous bromide of a trace of ferric salt would have lowered the atomic weight. The average of the two series, 55.877, must represent very closely the true atomic weight in question.

The value 55.88 for the atomic weight of iron thus receives fresh support. It is hardly conceivable that sufficient undiscovered impurity could have been present in the material used for either series of analyses to have affected the second figure of decimals. Nevertheless, further work on the subject is planned with the hope of increasing the purity of the material used for analysis.

Attention has been recently called to the possibility that the atomic weights of the magnetic metals might be affected by the attraction of the earth's magnetism. Obviously the error introduced by this weak attraction could not be large, but nevertheless the ascertaining of the order of inaccuracy is a point of some interest to the chemist.

The intensities of the earth's magnetic field in various places are well known, but the calculation of the attractive action of this field upon a given magnet depends, of course, upon the intensity and length of the magnet as well as upon the field. If the magnet is so short that its two poles are essentially the same distance from the earth's magnetic north pole, it is clear that the repelling effect of the earth upon one pole will practically counterbalance the attracting effect upon the other pole; hence the effect of the earth's magnetism will be simply directive, and

will have no attractive influence. Moreover, since the pure metals used in the atomic weight investigations upon iron, cobalt, and nickel in this laboratory were incapable of retaining magnetism, the earth's field will not have even a directive influence on these substances, but will only affect the polar direction of the weak induced magnetism.

If any further argument were needed as to the infinitesimal nature of the effect of the earth's magnetism upon the atomic weights in question, it might be found in the analytical results. Compounds are well known to be usually far less magnetic than the metals which they contain*; hence the magnetic attraction would increase the weight of the metal to a greater extent than that of the compound. But the complete analysis of the cobaltous and nickelous bromides accounted for all the material taken, without any considerable surplus, even although the metal was weighed in the elementary state. Hence, one concludes that the magnetic attraction must have been unimportant. Still, in order to prove the point directly, the following experiments were carried out.

The method of determination consisted in weighing iron in a normal fashion in the earth's magnetic field, and then weighing the iron again in a non-magnetic field, formed by neutralizing the earth's magnetism by means of a temporary magnet.

The vertical component of the earth's magnetism was, of course, the one which was to be eliminated; but if the magnet is placed in the line of the dipping needle, an intensity which would neutralize one component would also neutralize the other. Hence, the position of neutrality was determined by a horizontal needle or compass.

Upon the pan of a very sensitive balance was placed a small sensitive magnetic needle. The needle was then brought into an astatic condition by bringing near it one pole of a straight electro-magnet, thirty centimeters long, which was placed in a position as nearly as possible parallel with the lines of the earth's magnetic force. This electro-magnet consisted of a core of soft iron wire covered by six layers of stout copper wire. The magnetic attraction of the earth and of the electro-magnet neutralized each other when the distance of the electro-magnet from the needle was eighteen centimeters, and the current passing through it was 0.15 ampere.

The magnet was now removed and the compass replaced by a weighing bottle containing 6.7 grams of pure iron (reduced from the oxide by ignition in a current of hydrogen), which was then carefully counter-

* For example, see Plücker, *Pogg. Ann.*, 1848, 1851.

balanced with weights. Upon placing the electro-magnet in its former position and passing the same current through it as before, no perceptible difference in the weight of the iron could be observed. Two repetitions of the experiment gave the same result. Evidently the weight of iron is not influenced by the earth's magnetism to an extent which would necessitate the consideration of the permanent magnetic field even in the most accurate analytical work.

About ten grams of pure ferric oxide were now counterbalanced and the electro-magnet placed in a horizontal position so that one pole was directly below the weighing bottle and five centimeters distant from it. A much stronger current (0.4 ampere) was passed through the magnet, but no perceptible change in the weight of the oxide could be observed. The same result was obtained when the oxide was replaced by about the same quantity of bromide. When the metallic iron was placed upon the balance pan, an increase in weight of 0.0035 gram was produced by the magnet under the above conditions. The empty balance was not affected in the least by the magnet. It is easy to calculate from the figures given above that the vertical pull of the magnet upon the iron in the new position must be over a thousand times as great as it was in the more distant position. Hence it is not surprising that the magnet produced no change in the first experiment, for a difference in weight of 0.000003 gram could not have been detected.

To sum up the results of the investigation : —

1. The result for the atomic weight of iron previously obtained by analysis of the oxide, 55.88 ($O = 16.000$), was confirmed.
2. The specific gravity of ferrous bromide was found to be 4.636, at 25° referred to water at 4° .
3. The effect of the earth's magnetism on the weights of small quantities of the magnetic metals was shown to be negligible in even the most precise atomic weight work, as was to have been expected.

I wish to express my gratitude to Professor T. W. Richards for many friendly suggestions in the course of the work, especially in connection with the effect of terrestrial magnetism upon the weight of the magnetic metals. I am indebted to the Cyrus M. Warren Fund for Research in Harvard University for much of the necessary apparatus, and to Dr. Wolcott Gibbs for indispensable platinum vessels.

